

# FERRIHYDRITE - SCHWERTMANNITE - SILICATE MIXTURES AS A MODEL OF MARTIAN SOILS MEASURED BY PATHFINDER.

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The Imager for Mars Pathfinder (IMP) has produced numerous spectra of specific soil units near the mouth of the Ares and Tiu flood channels[1]. Selected IMP soil spectra are shown here and compared with spectra of synthetic soil analogs that resemble some of the spectral and chemical character of the Martian soils in this region. Spectral analysis of these samples includes determination of the  $T_1$  and  $T_2$  band centers and calculation of crystal field parameters. The results provide distinct distributions for the two groups of synthetic samples under study. Comparison of the spectra of these models to the soils measured by IMP suggest that a ferrihydrite-like component is a common pigmenting agent in these soils. The presence of the mineral schwertmannite in the Martian soils could account for some of the S and may be responsible for the angularity of the ~600 nm shoulder in some soil spectra. If magnetite is also a soil component it could be responsible for weakening the ~900 nm absorption characteristic of ferric oxides.

**Models.** The models used here are synthetically prepared aggregates of montmorillonite and iron oxide minerals and phases. Numerous samples have been prepared by adding  $FeCl_2$ ,  $FeCl_3$  or  $Fe_2(SO_4)_3$  to montmorillonite suspensions at pH 3-7 resulting in ferrihydrite-montmorillonite aggregates (Fe-monts) and ferrihydrite-schwertmannite-montmorillonite aggregates (FS-monts); these samples contain ~4 wt%  $Fe_2O_3$  as structural Fe in the clay, plus ~2-8 and 7-20 wt%  $Fe_2O_3$ , respectively, as ferric oxide in the Fe-monts and FS-monts [2]. The high Fe contents of the FS-mont samples resulted because sulfate facilitated  $Fe^{3+}$  uptake by the silicate and is higher than reasonable for Martian soil, thus giving stronger  $Fe^{3+}$  spectral features than would a similar soil with a Mars-like Fe abundance. Montmorillonite was used here both because it is a convenient and reactive template and because smectite clays are common weathering products and have been discussed as potential silicate phases in the Martian soil. Other layer silicates may also be present in the soil on Mars.

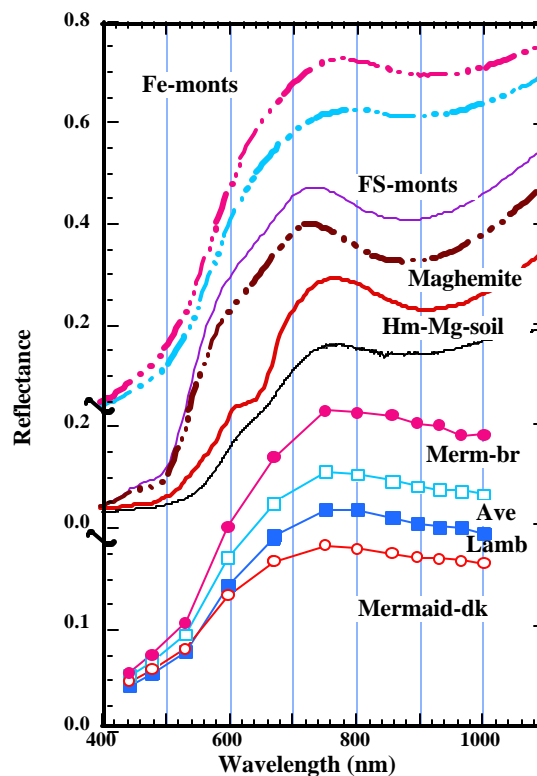
Ferrihydrite has been identified in the Fe-monts and both ferrihydrite and schwertmannite in the FS-monts using Mössbauer and reflectance spectroscopy; however, other less crystalline ferric oxide phases may be present as well [2]. Schwertmannite is a ferric oxyhydroxysulfate mineral [3].

**Spectra.** Shown in Fig. 1 are laboratory reflectance spectra of model soils and maghemite. Comparison of the Fe-mont soils to the FS-mont soils shows that the presence of schwertmannite causes a redshift of the reflectance maximum towards 720 nm and produces a more angular shoulder near 600 nm. The extended visible region spectra of schwertmannite very closely resemble those of the FS-mont samples shown here [4]. Spectra of maghemite and a hematite-magnetite-soil are included for comparison. The reflectance maximum for maghemite is near 760 nm and the shoulder near 600 nm is weaker than that of schwertmannite. Hematite

features in a natural soil appear to be weakened and broadened by the magnetite. This effect is under continued study.

The spectral bands for several Mars soils measured by IMP are shown in Fig. 1. Spectral corrections and processing have been performed on this data as described in [1,5]. The IMP soils shown here are (in order of decreasing brightness) bright soil 2 near "Mermaid" rock, an average of all IMP soil spectra, an average of 3 soils near "Lamb" rock, dark soil near "Mermaid" rock.

**Figure 1** Spectra of IMP Soils and Model Soils

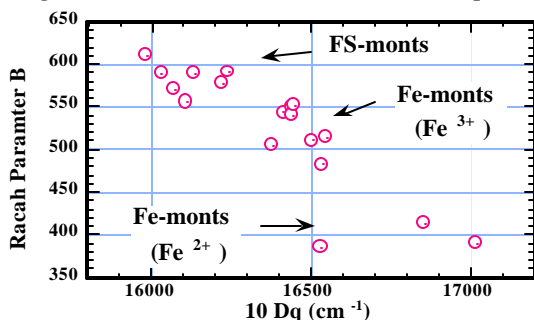


**Spectral analyses.**  $Fe^{3+}$  electronic transitions have been used to identify specific  $Fe^{3+}$  sites and discriminate among  $Fe^{3+}$  oxides [6,7,8]. The spectra of the model soils have been analyzed using cubic-spline second-derivatives as in [9] for the determination of band positions and calculation of the Racah B and C parameters (interelectronic repulsion energies) and 10 Dq (crystal field splitting energy) as in [8]. Plots of the  $T_1$  vs  $T_2$  band centers for 7 FS-monts and 11 Fe-monts showed clear separation of these two soils because the  $T_1$  and  $T_2$  bands each occur at shorter wavelengths for schwertmannite than for ferrihydrite.

A plot of the Racah-B and 10 Dq values for the model soils is shown in Fig. 2. A clear separation is observed here for the FS-mont and Fe-mont samples, as well as further separation of the Fe-mont group that correlates well with the

Fe oxidation state during synthesis. Although the Fe-mont and FS-mont soils are prepared similarly, differences in their  $\text{Fe}^{3+}$  mineralogies can be determined spectrally and may be related to the differences in  $\text{Fe}^{3+}$  mineralogy observed for the IMP soils.

Figure 2 Distribution of Fe-treated mont samples



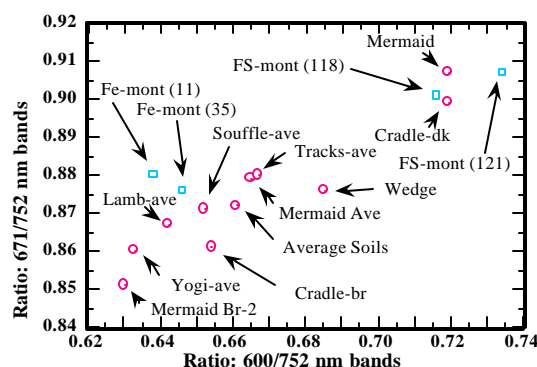
The spectral analyses of the Martian soils presented here are focussed on the shape of the 600 nm shoulder and the degree of curvature from 600 to 670 to 750 nm. Ratios were calculated of the 670 to 750 nm bands and 600 to 750 nm bands. A plot of these ratios is shown in Fig. 3. Similar ratios were determined for the model soils and examples of the Fe-monts and FS-monts are shown in Fig. 3. Variations in the angularity of the 600 nm shoulder are shown here, where the dark soils near “Mermaid” and “Cradle” exhibit a more angular shoulder like that observed for schwertmannite-bearing soils, whereas soils near “Lamb” and “Souffle” exhibit a more rounded curvature from 600-670-750 nm similar to the spectral character of ferrihydrite-bearing soils. Similar ratios for other ferric oxides such as hematite and maghemite occur in the direction of the “Yogi” soils and the bright soil near “Mermaid”, but are far off the scale of Fig. 3. Complete spectral analysis of the Martian soils measured by IMP requires consideration of many other spectral features, which are dealt with elsewhere [5].

Variations in the chemical abundances of these soils indicate a good correlation of wt%  $\text{SO}_3$  with 750/440 nm band ratios [10]. This suggests that the ferric mineral(s) responsible for the reflectance maximum near 750 nm are correlated with sulfates in the soils. This would be consistent with the presence of a schwertmannite-like component, but is only one of many interpretations.

These Martian soils are thought to contain impure forms of the minerals maghemite and possibly magnetite [11]. It is thus reasonable to consider how the presence of magnetite and maghemite would influence the spectra of the Fe-mont and FS-mont soils. Linear spectral mixtures containing up to 10% magnetite and maghemite produce only small decreases in reflectance and little change in spectral band shape for the Fe-mont and FS-mont spectra. Spectral analysis of physical mixtures of these materials is underway and may produce a more pronounced influence on these spectra. Spectral analysis of natural magnetite- and maghemite-bearing soils show that even trace amounts of magnetite in soils may broaden the

$T_1$  absorption feature near 0.9  $\mu\text{m}$  and cause a negative NIR continuum slope [9].

Figure 3 Spectral ratios of IMP soils and model soils



**Applications to Mars.** The spectral character of many of the Martian soils measured by IMP contains a reflectance maximum near 800 nm that is consistent with ferrihydrite and variability in the shape of the 600 nm shoulder feature that would be consistent with variable abundance of a schwertmannite-like component. Preliminary analyses indicate that adding the ~6% maghemite estimated for the IMP soils [11] would not greatly alter the spectral character of these samples. A natural mixture containing magnetite and these model soils could weaken the 0.9  $\mu\text{m}$  band and decrease the brightness. Because ferrihydrite exhibits spectral properties similar to the Martian soils measured by IMP does not require the presence of ferrihydrite in the soils on Mars. Spectral features in the extended visible region are insufficient alone to uniquely distinguish between all ferric oxide phases [9]. A np ferric oxide that exhibits some hematite properties appears to have a similar spectral character to ferrihydrite [12]. XRD and 4 K Mössbauer measurements (*in situ* or on returned samples) will be necessary for unique mineral identification. Low-temperature dehydration of ferrihydrite has not been studied in detail and may produce a more stable np ferric oxide phase that could have persisted on Mars until today. Ferrihydrite-like phases have been identified in volcanic soils and are thought to be responsible for their Mars-like spectral properties [13].

**References.** 1 Smith P. *et al.* (1997) *Science*, 278, 1758. 2 Bishop, J. *et al.* (1995) *Icarus*, 117, 101. 3 Bigham J. *et al.* (1990) *GCA*, 54, 2743; Schwertmann U. *et al.* (1995) *Eur. J. Min.*, 7, 547. 4 Bishop, J. & E. Murad (1996) in *Min. Spectr.*, The Geochem. Soc., 337. 5 Bell J. F. III *et al.* (1998) LPSC - this issue; Morris R. pers. comm. 6 Sherman D. & T. Waite (1985) *Am. Min.*, 70, 1262. 7 Morris R. *et al.* (1985) *JGR*, 90, 3126. 8 Scheinost A. & U. Schwertmann (1997) *LPSC XXVIII*, 1243. 9 Scheinost A. *et al.* (1998) *CCM*, submitted. 10 Bridges N. *et al.* (1998) LPSC - this issue; Rieder R. *et al.* (1997) *Science*, 278, 1771. 11 Hviid S. *et al.* (1997) *Science*, 278, 1768. 12 Morris R. *et al.* (1989) *JGR*, 94, 2760. 13 Morris R. *et al.* (1993) *GCA*, 57, 4597; Bishop J. *et al.* (1998) *JGR*, submitted.

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